

# COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

*The Synthesis, Reactions and Structures  
of Organometallic Compounds*

*Editor*

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*The Synthesis, Reactions and Structures of  
Organometallic Compounds*

**Volume 4**

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# **COMPREHENSIVE ORGANOMETALLIC CHEMISTRY**

# Preface

Although the discovery of the platinum complex that we now know to be the first  $\pi$ -alkene complex,  $K[PtCl_3(C_2H_4)]$ , by Zeise in 1827 preceded Frankland's discovery (1849) of diethylzinc, it was the latter that initiated the rapidly developing interest during the latter half of the nineteenth century in compounds with organic groups bound to the elements. This era may be considered to have reached its apex in the discovery by Grignard of the magnesium reagents which occupy a special place because of their ease of synthesis and reactivity. With the exception of trimethylplatinum chloride discovered by Pope, Peachy and Gibson in 1907 by use of the Grignard reagent, attempts to make stable transition metal alkyls and aryls corresponding to those of main group elements met with little success, although it is worth recalling that even in 1919 Hein and his co-workers were describing the 'polyphenylchromium' compounds now known to be arene complexes.

The other major area of organometallic compounds, namely metal compounds of carbon monoxide, originated in the work starting in 1868 of Schützenberger and later of Mond and his co-workers and was subsequently developed especially by Hieber and his students. During the first half of this century, aided by the use of magnesium and, later, lithium reagents the development of main group organo chemistry was quite rapid, while from about 1920 metal carbonyl chemistry and catalytic reactions of carbon monoxide began to assume importance.

In 1937 Krause and von Grosse published their classic book 'Die Chemie der Metallorganischen Verbindungen'. Almost 1000 pages in length, it listed scores of compounds, mostly involving metals of the main groups of the periodic table. Compounds of the transition elements could be dismissed in 40 pages. Indeed, even in 1956 the stimulating 197-page monograph 'Organometallic Compounds' by Coates adequately reviewed organo transition metal complexes within 27 pages.

Although exceedingly important industrial processes in which transition metals were used for catalysis of organic reactions were developed in the 1930s, mainly in Germany by Reppe, Koch, Roelen, Fischer and Tropsch and others, the most dramatic growth in our knowledge of organometallic chemistry, particularly of transition metals, has stemmed from discoveries made in the middle years of this century. The introduction in the same period of physical methods of structure determination (infrared, nuclear magnetic resonance, and especially single-crystal X-ray diffraction) as routine techniques to be used by preparative chemists allowed increasingly sophisticated exploitation of discoveries. Following the recognition of the structure of ferrocene, other major advances quickly followed, including the isolation of a host of related  $\pi$ -complexes, the synthesis of a plethora of organometallic compounds containing metal-metal bonds, the characterization of low-valent metal species in which hydrocarbons are the only ligands, and the recognition from dynamic NMR spectra that ligand site exchange and tautomerism were common features in organometallic and metal carbonyl chemistry. The discovery of alkene polymerization using aluminium alkyl-titanium chloride systems by Ziegler and Natta and of the Wacker palladium-copper catalysed ethylene oxidation led to enormous developments in these areas.

In the last two decades, organometallic chemistry has grown more rapidly in scope than have the classical divisions of chemistry, leading to publications in journals of all national chemical societies, the appearance of primary journals specifically concerned with the topic, and the growth of annual review volumes designed to assist researchers to keep abreast of accelerating developments.

Organometallic chemistry has become a mature area of science which will obviously continue to grow. We believe that this is an appropriate time to produce a comprehensive review of the subject, treating organo derivatives in the widest sense of both main group and transition elements. Although advances in transition metal chemistry have appeared to dominate progress in recent years, spectacular progress has, nevertheless, also been made in our knowledge of organo compounds of main group elements such as aluminium, boron, lithium and silicon.

In these Volumes we have assembled a compendium of knowledge covering contemporary organometallic and carbon monoxide chemistry. In addition to reviewing the chemistry of the ele-



ments individually, two Volumes survey the use of organometallic species in organic synthesis and in catalysis, especially of industrial utility. Within the other Volumes are sections devoted to such diverse topics as the nature of carbon-metal bonds, the dynamic behaviour of organometallic compounds in solution, heteronuclear metal-metal bonded compounds, and the impact of organometallic compounds on the environment. The Volumes provide a unique record, especially of the intensive studies conducted during the past 25 years. The last Volume of indexes of various kinds will assist readers seeking information on the properties and synthesis of compounds and on earlier reviews.

As Editors, we are deeply indebted to all those who have given their time and effort to this project. Our Contributors are among the most active research workers in those areas of the subject that they have reviewed and they have well justified international reputations for their scholarship. We thank them sincerely for their cooperation.

Finally, we believe that 'Comprehensive Organometallic Chemistry', as well as providing a lasting source of information, will provide the stimulus for many new discoveries since we do not believe it possible to read any of the articles without generating ideas for further research.

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## Manganese

P. M. TREICHEL

University of Wisconsin-Madison

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## 29.1 INTRODUCTION

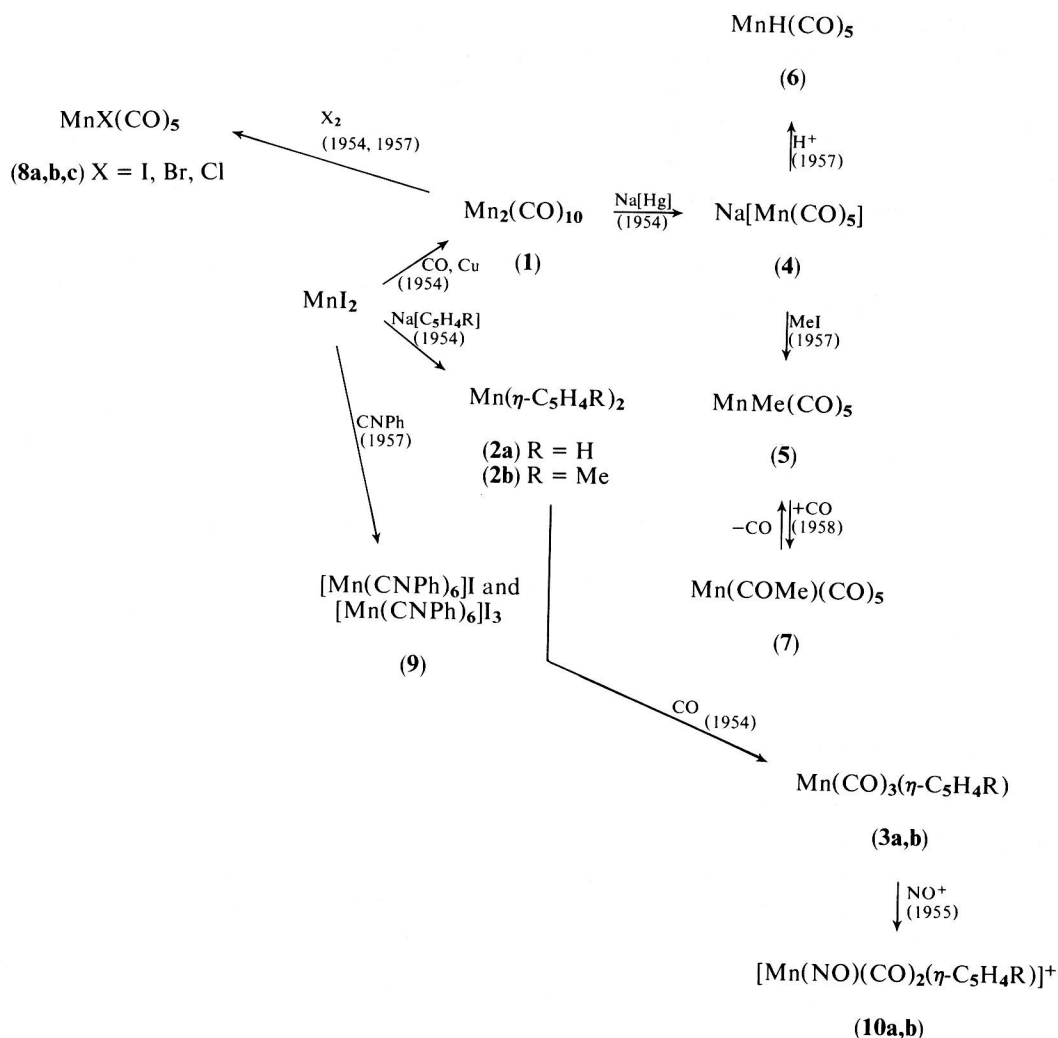
### 29.1.1 Historical Perspective

Unlike the organometallic chemistry of most other transition metals, the organometallic chemistry of manganese does not have a particularly extensive history. There are several incomplete and unsubstantiated reports of phenylmanganese species in the late 1930s and early 1940s, but the development of the organometallic chemistry of this element dates essentially from 1954. Thus the origins of organomanganese chemistry are found in the time following the discovery of ferrocene, and development of this area has been in step with the rapid expansion of modern organometallic chemistry. Significant references to the early work in this area are provided in Table 1. Scheme 1 provides a summary of these early studies.

**Table 1** The Early Development of the Organometallic Chemistry of Manganese

Date	Subject	Ref.
1937, 1941	Reference to $Mn(C_6H_5)_2$ and $Mn(C_6H_5)I$ , uncharacterized products from $MnI_2 + C_6H_5MgBr$	1, 2
1949	First reference to $Mn_2(CO)_{10}$ , fully characterized in 1954	3, 4
1954	Preparation of $MnI(CO)_5$ , $Na[Mn(CO)_5]$	4
	Preparation of $Mn(\eta-C_5H_5)_2$	5, 6
	Preparation of $Mn(CO)_3(\eta-C_5H_5)$	6, 7
1955	Preparation of $[Mn(NO)(CO)_2(\eta-C_5H_5)]^+$	8
1956	Preparation of $[Mn(CNR)_6]^+$ complexes	9
1957	Preparation of $MnCH_3(CO)_5$	10
	Preparation of $MnH(CO)_5$	11

- H. Gilman and J. C. Bailie, *J. Org. Chem.* 1937, **2**, 84.
- H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, 1941, **63**, 2046.
- D. T. Hurd, G. W. Sentell, Jr. and F. J. Norton, *J. Am. Chem. Soc.*, 1949, **71**, 1899.
- E. O. Brimm, M. A. Lynch, Jr. and W. J. Sesny, *J. Am. Chem. Soc.*, 1954, **76**, 3831.
- G. Wilkinson and F. A. Cotton, *Chem. Ind. (London)*, 1954, 307.
- E. O. Fischer and R. Jira, *Z. Naturforsch., Teil B*, 1954, **9**, 618.
- G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. Chem.*, 1956, **2**, 95.
- T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1955, **1**, 165.
- A. Sacco, *Gazz. Chim. Ital.*, 1956, **86**, 201.
- R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, 1957, **22**, 598.
- W. Hieber and G. Wagner, *Z. Naturforsch., Teil B*, 1957, **12**, 478.



Scheme 1

It appears that dimanganese decacarbonyl (1) was the first organometallic compound of manganese to be isolated and characterized. This compound was, however, one of the last of the simple metal carbonyls to be discovered, being first isolated and identified in 1949 and not adequately characterized in the chemical literature until 1954. This contrasts with the early discovery of carbonyl complexes of the adjacent elements in the periodic table,  $\text{Cr(CO)}_6$ ,  $\text{Fe(CO)}_5$ ,  $\text{Co}_2(\text{CO})_8$  and  $\text{Ni(CO)}_4$ , all of which were reported in the late 1800s and early 1900s. In fact, even the discovery of dirhenium decacarbonyl preceded the first report on (1) by about a decade.

Manganocene, bis(cyclopentadienyl)manganese (2a), was prepared and characterized in the research groups of Wilkinson and Fischer in 1954; these reports followed, by a few years, the discovery of ferrocene. This compound was found to be rather atypical among the metallocenes, being a high-spin 'ionic' compound, and it has only been in recent years that structural and magnetic studies on (2a) and on other substituted manganocenes have been interpreted fairly completely. Shortly after the discovery of manganocene it was determined that this compound could be converted to cyclopentadienylmanganese tricarbonyl (3a) by treatment with CO under pressure. An extensive organic chemistry was developed around this compound, which was found to behave rather like ferrocene, showing a proclivity towards aromatic-type reactions at the cyclopentadienyl ligand. A closely related complex, methylcyclopentadienylmanganese tricarbonyl (3b), has been produced commercially for use as an antiknock agent for gasoline. As a consequence, compound (3b) is currently available cheaply and in large quantity; this has surely contributed to the extensiveness of study accorded this species.

The reduction of (1) by sodium amalgam was reported in 1954, the product obtained *in situ* being  $\text{Na[Mn(CO)}_5]$  (4). This carbonylmetallate anion is an important precursor for the formation



of various other manganese carbonyl derivatives, including  $\text{MnMe}(\text{CO})_5$  (**5**) and  $\text{MnH}(\text{CO})_5$  (**6**). Much further study has been built around compound (**5**), including the formation of compound (**7**) by the insertion reactions of a CO molecule into the metal-carbon  $\sigma$ -bond. Compound (**5**) is the first authenticated compound with a manganese-carbon  $\sigma$ -bond. However, it should be mentioned that in a 1937 journal article the reaction of phenylmagnesium bromide and manganese(II) iodide was reported. It was suggested that the dark colored product of this reaction contained both phenylmanganese iodide and diphenylmanganese, but unfortunately the characterization of these species was inadequate. Much later, diphenylmanganese was characterized as a green crystalline species, formed from  $\text{MnI}_2$  and phenyllithium. Dimethylmanganese and methylmanganese iodide were identified at the same time. Much more significant study of this area, which has produced other dialkylmanganese compounds, has been carried out in recent years. This work is, of course, a part of the broad effort in organometallic chemistry concerned with homoleptic metal alkyls.

Manganese pentacarbonyl iodide (**8a**) was characterized in 1954; this compound was formed by carbonylation of  $\text{MnI}_2$ . Only somewhat later were preparations of this compound and the other manganese pentacarbonyl halides,  $\text{MnBr}(\text{CO})_5$  (**7b**) and  $\text{MnCl}(\text{CO})_5$  (**8c**), accomplished by cleavage of the metal-metal bond in (**1**) by halogens. Compounds (**8a-c**) have also served as important synthetic precursors in many studies on organomanganese compounds.

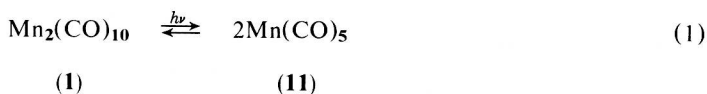
Other significant early developments in the organometallic chemistry of manganese include the preparations of various isocyanide complexes,  $[\text{Mn}(\text{CNR})_6]^+$  (**9**), from  $\text{MnI}_2$  and organic isocyanides, and the characterization of the first nitrosyl complex,  $[\text{Mn}(\text{NO})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^+$  (**10a**). Further work has extended the number of manganese isocyanide and nitrosyl complexes so that many complexes having these ligands are now known.

### 29.1.2 Introductory Comments

The history of this area of manganese organometallic chemistry presented above, although not extensive, still provides a sort of general perspective for this review. This topic is generally dominated by carbonyl containing complexes. Complexes having as ligands only hydrocarbon or alkyl groups or isocyanides, and lacking carbonyl groups, are far less abundant although the chemistry of these species is no less interesting.

As with all carbonyl containing complexes, manganese carbonyl complexes exist only within a fairly rigid set of guidelines. Almost all manganese carbonyl species are 18-electron, or EAN rule obeying, complexes and as a consequence they are diamagnetic. In order for carbonyl complexes to be stable, fairly low metal formal oxidation states are required. Only in low oxidation state complexes is stability of the metal-carbonyl bond achieved, since this allows substantial  $\pi$ -bonding between metal and ligand. Carbonyl complexes, if there is no overall charge and counterion, exhibit characteristics typical of covalent compounds such as volatility, low melting point, and solubility in organic solvents.

A noteworthy exception to EAN rule chemistry is a group of monomeric manganese(0) species having a  $d^7$  configuration. These include the complex  $\text{Mn}(\text{CO})_5$  (**11**), generated when (**1**) is photolyzed (equation 1). This complex is itself unstable with respect to (**1**); it may be studied only as a transient intermediate or trapped and stabilized in a chemical reaction. The radical species (**11**) has been found to have unique chemical behavior, including a high susceptibility to carbonyl loss.



Manganese in its organometallic chemistry typically assumes formal oxidation states of  $-1$ ,  $0$  and  $+1$ . Complexes in the divalent state are known in certain instances; for example, in isocyanide chemistry the divalent complexes  $[\text{Mn}(\text{CNR})_6]^{2+}$  have been characterized as oxidation products of  $[\text{Mn}(\text{CNR})_6]^+$ . The  $+1$  oxidation state is particularly noteworthy, for such complexes have the very stable  $3d^6$  electron configuration. Spin paired octahedral complexes having this configuration are abundant. The  $-1$  oxidation state ( $3d^8$ ) is limited to derivatives of the trigonal bi-

pyramidal pentacarbonylmanganate ion. In the zerovalent state ( $3d^7$ ) most complexes [e.g.  $\text{Mn}_2(\text{CO})_{10}$ ] are dimeric.

For carbonyl containing complexes, carbonyl stretching frequencies,  $\nu(\text{CO})$ , are commonly recorded. These data are used to predict or verify molecular structures and also to provide information on the electronic properties of associated ligands. NMR spectra are often reported, and these data have been used for structure elucidation and to study molecular dynamics and reaction rates. Mass spectrometry has been used as an analytical tool with volatile complexes, the mass of the parent ion and the fragmentation pattern being characteristic of the identity and structure of such species. ESR studies have played an important role in recent study of radical species.

### 29.1.3 Other Literature

There is very little literature (books, review articles, *etc.*) which is directed solely to the organometallic chemistry of manganese. The chapter on manganese in 'Comprehensive Inorganic Chemistry'<sup>1</sup> contains a brief section on the organometallic chemistry of this element. A review article on manganese carbonyl chemistry was written in 1968,<sup>2</sup> but this is generally not available. The first chapter of the book 'Organic Synthesis via Metal Carbonyls'<sup>3</sup> is a general review of metal carbonyl chemistry and contains significant information on carbonyl compounds of manganese, but this is now quite old. The best sources from which to obtain a detailed summary of the work in this area, presented on a year to year basis, are the Annual Surveys articles published by Elsevier. The first three surveys from 1964, 1965 and 1966 were published as books under the title 'Annual Survey of Organometallic Chemistry'.<sup>4</sup> Articles from 1966–1970 appeared bound separately in a Journal format, under the title 'Organometallic Chemistry Reviews'.<sup>5</sup> Since 1971, Annual Surveys of Manganese, Technetium and Rhenium have appeared approximately yearly in the *Journal of Organometallic Chemistry*.<sup>6</sup> This author has written these articles since 1972.

A few topical reviews are available. These are individually referenced at the appropriate place in this article.

Documented, detailed preparations of quite a number of organomanganese compounds are given in *Inorganic Syntheses*. These are listed in Table 2.

**Table 2** Preparations of Organomanganese Compounds Described in *Inorganic Syntheses*

Compound	Authors	Volume	Page
$\text{Na}[\text{Mn}(\text{CO})_5]$ , <i>in situ</i>	R. B. King, F. G. A. Stone	7	198–201
$\text{MnH}(\text{CO})_5$	R. B. King, F. G. A. Stone	7	198–201
$\text{Mn}(\text{SnMe}_3)(\text{CO})_5$	R. E. J. Bichler, M. R. Booth, H. C. Clark, B. K. Hunter	12	60–62
$\text{Mn}_3\text{H}_3(\text{CO})_{12}$	B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson	12	43–45
$[\text{Mn}(\text{NO})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$	N. G. Connelly	15	91–92
$\text{Mn}(\text{GeH}_3)(\text{CO})_5$	S. R. Stobart	15	174–176
$\text{Mn}(\text{CO})(\text{NO})_3$	S. K. Satija, B. I. Swanson	16	4–5
$\text{Mn}(\text{CO})_2(\text{CS})(\eta\text{-C}_5\text{H}_5)$	I. S. Butler, N. J. Coville, A. E. Fenster	16	53–55
$\text{Ti}[\text{Mn}(\text{CO})_5]_3$	A. T. T. Hsieh, M. J. Mays	16	61–63
$\text{Mn}(\text{COMe})(\text{CO})_5$	C. M. Lukehart, G. P. Torrence, J. V. Zeile	18	57–58
$\text{Al}[\text{Mn}(\text{CO})_4(\text{COMe})_2]_3$	C. M. Lukehart, G. P. Torrence, J. V. Zeile	18	58–60
$\text{MnCl}(\text{CO})_5$	K. J. Reimer, A. Shaver	19	159–160
$\text{MnX}(\text{CO})_5$ (X = Br, I)	M. H. Quick, R. J. Angelici	19	160–162
$\text{MnI}(\text{CO})_5$ (alternate procedure)	K. J. Reimer, A. Shaver	19	162–163
$\text{Mn}(\text{CO})(\text{CS})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$	I. S. Butler, N. J. Coville, D. Cozak, S. R. Desjardins, A. E. Fenster, K. R. Plowman	19	189–191
$\text{Mn}(\text{dppe})(\text{CS})(\eta\text{-C}_5\text{H}_5)$	I. S. Butler, N. J. Coville, D. Cozak, S. R. Desjardins, A. E. Fenster, K. R. Plowman	19	193–197
$\text{Mn}(\text{B}_3\text{H}_8)(\text{CO})_4$	S. J. Hildebrand, D. F. Gaines	19	227–231
$\text{Mn}(\eta^1\text{-C}_5\text{H}_4\text{X})(\text{CO})_5$ (X = Cl, Br, I)	K. J. Reimer, A. Shaver	20	188–193
$\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{X})(\text{CO})_5$ (X = Cl, Br)	K. J. Reimer, A. Shaver	20	193–194
$\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{Cl}_4\text{X})$ (X = Cl, Br)	K. J. Reimer, A. Shaver	20	194–196
$\text{Mn}_3\text{H}(\text{B}_2\text{H}_6)(\text{CO})_{10}$	H. D. Kaesz, S. W. Kirtley	20	240–242